

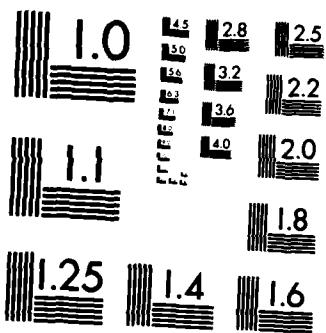
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NRL Memorandum Report 5416

Localized Ionic Currents from a Corroding Iron-Copper Galvanic Couple

C. R. CROWE

*Composite Materials Branch
Material Science and Technology Division*

AD-A153 627

April 18, 1985

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<p>In this report, progress in the application and development of scanning vibrating electrode techniques (SVET) for electrochemical measurements needed to test finite element models is presented. The test system is an iron-copper galvanic couple in which SVET have been used to measure local ionic currents in solution with spatial and current resolutions of the order of 15 to 20 μm and 5nA/cm², respectively. Thus, it is possible to measure corrosion currents resulting from individual local cell activity on a scale sufficient to test finite element models (FEM) for accuracy.</p>			
<p>The report covers a) a review of the state-of-the-art of scanning vibrating probe techniques, b) an experimental evaluation of the one-dimensional probe technique as applied to planar galvanic couple between iron and copper, and c) a discussion of the development of a three-dimensional probe to advance the state-of-the-art.</p>			
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19. ABSTRACT (continued)

Based on the completed experimental electric field scans and the corresponding finite element field prediction, it appears that the finite element technique presents a strong analytical tool for calculating the near field electric field distributions about active electrode surfaces in homogeneous media.

Additional figures to : matrix matrix computation

CONTENTS

INTRODUCTION	1
SCANNING VIBRATING PROBE TECHNIQUES - REVIEW OF THE STATE-OF-THE-ART	2
EXPERIMENTAL EVALUATION OF THE ONE-DIMENSIONAL PROBE TECHNIQUE	5
Materials	5
Electrochemical Measurements	5
RESULTS AND DISCUSSION	7
Electrochemical Measurements	7
Limitations of the Methods	14
DEVELOPMENT OF A THREE DIMENSIONAL PROBE	16
ACKNOWLEDGMENTS	17
REFERENCES	18

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LOCALIZED IONIC CURRENTS FROM A CORRODING IRON-COPPER GALVANIC COUPLE

INTRODUCTION

The characterization of localized corrosion phenomena such as pitting and crevice corrosion has been the focus of study for many years.¹⁻³ It is generally agreed that electrogalvanic interactions of anodic and cathodic regions inherent in real world physical systems are very complex processes. This is particularly true in view of the highly interactive coupling which exists between multiple anodes and cathodes subject to geometric effects, inhomogeneous electrolytic media, and polarization effects.

A number of attempts have been made to model localized corrosion using detailed models of the electrochemistry in localized regions. The idea of mathematically predicting the electrolytic corrosion behavior for a physical situation began with the work of Wagner at least four decades ago.⁴ In this pioneering work, traditional mathematical techniques were applied to predict the potential fields of anodes and cathodes when considering the geometric effects, polarization, and surface roughness. Analytical attempts to calculate local current distributions in the anodic/cathodic neighborhood (surfaces) generated immediate realizations that, in general, exact mathematical solutions seemed intractable except in highly specialized situations where the equations could be solved for particular geometry and electrochemical situations.⁴⁻⁹ Thus the analytical models were limited in part to simple geometries and constant electrolyte properties. Furthermore the models were limited because the analyses did not take into account geometric changes of the electrode due to corrosion nor did they consider changes in composition and conductivity of the electrolyte during the course of corrosion.

In recent years studies have been conducted which apply finite element numerical techniques to macroscopic electrogalvanic field predictions. These models were developed for the prediction of performance of cathodically protected structures.¹⁰⁻¹³ Although the models did not consider changes in geometry and electrolyte properties, they were very successful in predicting current distributions at the various anodic and cathodic areas.

In order to effectively use the finite element models (FEM), sufficient electrochemical data must be measured under controlled conditions to compare model predictions with reality and to establish a data base of appropriate information. First, potential field measurements at localized areas are needed to compare finite element predictions with actual potential fields and the resultant ionic currents. The basic problem is to measure ionic currents associated with corrosion microcells. Secondly, potentiostatic polarization

and impedance measurements are required as a function of electrolyte chemistry. This information is needed to update the evolution of the electrochemical system parameters with time.

Recent advances in techniques of measuring localized currents in solutions have made possible methods to measure ionic currents associated with corrosion microcells. The new techniques use vibrating probes to measure currents in solution with spatial and current resolutions of the order of 15 to 20 μm and 5nA/cm^2 , respectively. Thus, it is possible to measure corrosion currents resulting from individual local cell activity on a scale closely related to many microstructural features of materials. This is particularly useful for studying of localized corrosion phenomena such as pitting and crevice corrosion and corrosion of composites where local galvanic effects between constituents and interfaces may be important.¹⁴

In this report, progress in the application and development of scanning vibrating electrode techniques (SVET) for electrochemical measurements needed to test finite element models is presented. The report covers a) a review of the state-of-the-art of scanning vibrating probe techniques, b) an experimental evaluation of the one-dimensional probe technique as applied to planar galvanic couple between iron and copper, and c) a discussion of the development of a three-dimensional probe to advance the state-of-the-art.

SCANNING VIBRATING PROBE TECHNIQUES - REVIEW OF THE STATE-OF-THE-ART

Historically, the vibrating probe techniques were developed for biological studies¹⁵⁻¹⁷ but have recently been used to study corrosion phenomena.¹⁸ Jaffe and his co-workers developed a one-dimensional vibrating microprobe that demonstrated the methodology. The microprobe operates by oscillating a single electrode along a line and measuring the time-varying potential of the electrode relative to a fixed, distant reference electrode. The vibrating electrode is a small metal sphere 10 μm to 30 μm in diameter which is vibrated between two points typically 10 μm to 30 μm apart. The voltage at the two extremes of vibration is measured and used to calculate the current density component in the medium at the center of and along the axis of vibration by the relation

$$J (\text{A/cm}^2) = \sigma (\Omega \cdot \text{cm})^{-1} \Delta V (\text{volts}) / \Delta r (\text{cm}) \quad (1)$$

where J is the current density component parallel to the probe vibration, ΔV is the voltage difference between the extremes of vibration, Δr is the vibration stroke, and σ is the conductivity of the solution.

The corrosion current density component normal to the surface or the net ion flux crossing the volume of material sampled by the probe at any specific region can be directly measured by vibrating the probe normal to the corroding surface just outside the corrosion cell. The local corrosion current density is then obtained by adjusting for the field fall-off between the surface and the center of probe vibration using an appropriate extrapolation procedure.

The electrode achieves high sensitivity by setting the oscillation at a frequency, f , where the $1/f$ noise is negligible. The basic principle for achieving high sensitivity is shown schematically in Fig. 1a. A lock-in amplifier is used to restrict the measuring bandwidth to a small range of frequencies centered about the oscillation frequency. The rapidity of the movement of the probe results in the potential being sampled at two points, V_{p1} and V_{p2} , before the electrode noise has changed appreciably. This produces a high sensitivity measurement that is several orders of magnitude more sensitive than has been obtained by the more conventional method of translating a non-vibrating probe relative to a second fixed reference.¹⁹ Because the translated electrode is moved slowly with respect to the high frequency components of the electrode noise, the ΔV noise is large (Fig. 1b).

Ishikawa and Isaacs¹⁸ have adapted the one-dimensional vibrating probe method to study pitting corrosion of aluminum alloys. They have developed a scanning technique whereby the vibrating probe is held in a mechanical stage driven by two stepping motors arranged to scan in the X-Y plane which is parallel to the surface of the specimen. The probe vibrates in the Z direction for measurements of current density normal to the surface of the specimen, J_z . By applying a potentiodynamic ramp to the specimen and measuring the current response of the ions streaming from active pits, Ishikawa and Isaacs were able to develop localized polarization curves for pits and surrounding regions.

Freeman, et al,¹⁶ have developed a two-dimensional technique. In their method, a single electrode is rotated rapidly (300 Hz) in a small ($15\mu m$) circle. The circular movement of the microelectrode is controlled by sine and cosine voltages generated by a computer. These signals are applied to two miniature loudspeakers mounted at right angles. A platinized tungsten microelectrode is attached to the intersection of rods extending from each speaker. The microelectrode voltage $\phi(X,Y)$ is sensed by an ultra-low-noise amplifier at each of 256 points around the circular path. The data is stored in a buffer memory in a dedicated microcomputer interfaced with voltage measurement circuitry. The current density is measured in the plane of rotation. Because the potential is measured around a circle, it is possible to determine two orthogonal components of the current density simultaneously. Again, the rapidity of the motion greatly reduces the effect of $1/f$ noise generated by the electrode and produces a high sensitivity current measurement.

In addition, Freeman, et al¹⁶ have developed an algorithm that allows the gradients as well as the two current density components to be measured. The gradients are important in FEM and therefore this algorithm provides another set of data which could not hitherto be obtained. The observed voltage from the rotating electrode is represented by a Taylor's series expansion about the central point (X_0, Y_0) of the circle of radius r

$$\phi(X,Y) = \phi(X_0, Y_0) + \frac{\partial\phi}{\partial X}(X-X_0) + \frac{\partial\phi}{\partial Y}(Y-Y_0) \quad (2a)$$

$$= \phi(X_0, Y_0) + r\cos\theta \left. \frac{\partial\phi}{\partial X} \right|_{(X_0, Y_0)} + r\sin\theta \left. \frac{\partial\phi}{\partial Y} \right|_{(X_0, Y_0)} \quad (2b)$$

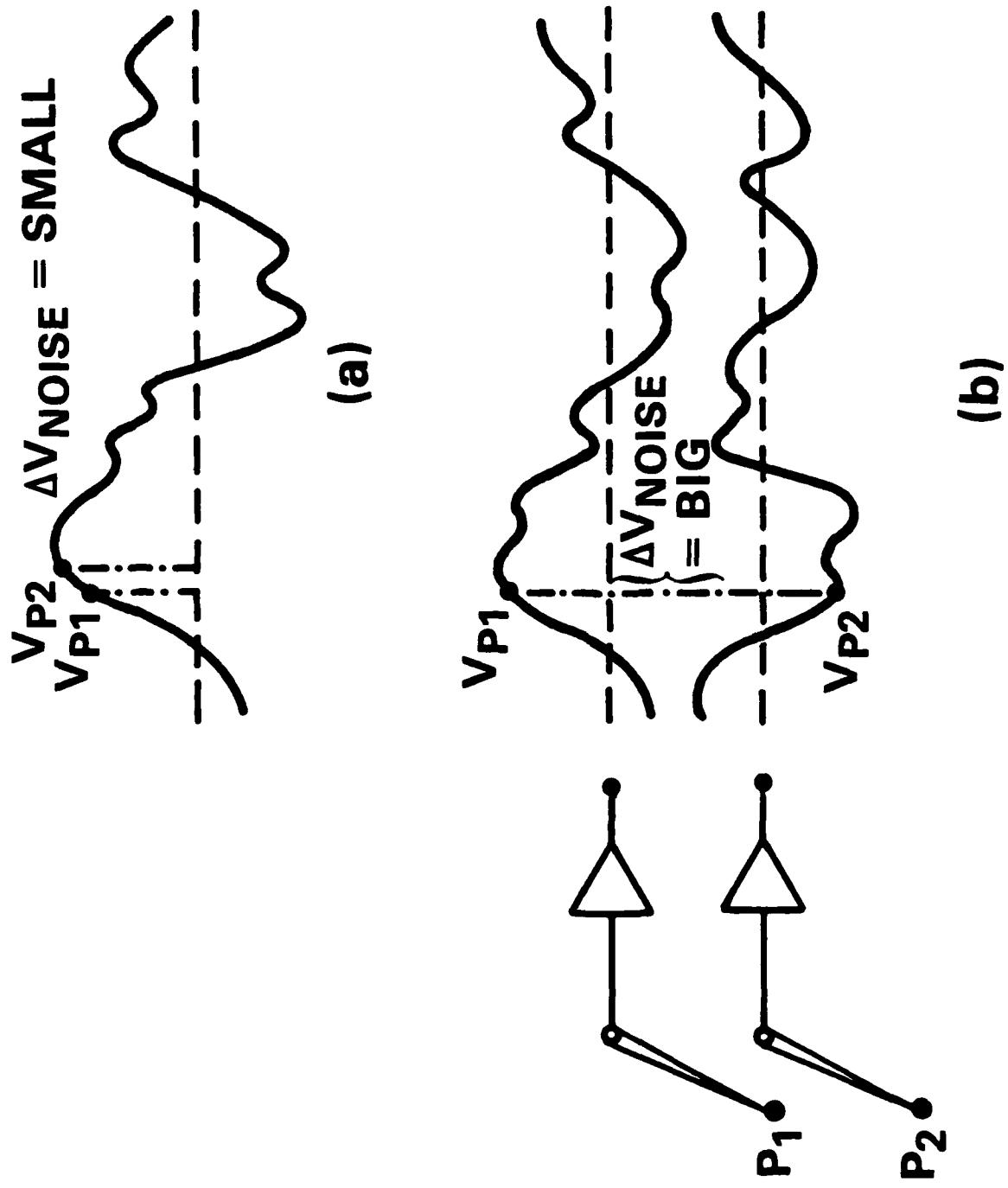


Fig. 1 - Schematic showing signal noise reduction achieved by using a) vibrating electrodes compared with
b) static electrodes

where $(X-X_0) = r\cos\theta$, $(Y-Y_0) = r\sin\theta$ and the partial derivatives are evaluated at (X_0, Y_0) . The current density at the central point (X_0, Y_0) has components J_x and J_y given by the convolution integrals

$$J_x = -\frac{\sigma}{r} \int_0^{2\pi} V(\theta) \cos\theta d\theta \quad (3)$$

$$J_y = -\frac{\sigma}{r} \int_0^{2\pi} V(\theta) \sin\theta d\theta \quad (4)$$

where σ is the conductivity of the medium at (X_0, Y_0) . The microcomputer evaluates these integrals for 1000 or more cycles of the probe and then averages the current densities and calculates the gradients. Using this technique, current density sensitivity as low as 5 nA/cm^2 has been obtained.

EXPERIMENTAL EVALUATION OF THE ONE-DIMENSIONAL PROBE TECHNIQUE

The application of the one-dimensional scanning vibrating electrode technique developed by Isaacs at the Brookhaven National Laboratory to galvanic corrosion of an iron-copper galvanic couple was studied. The experiment was performed using an Fe/Cu galvanic couple with a geometry which would allow a direct comparison of the measurement with the FEM predictions of Kasper and Duffy²⁰ and could also be related to the analytical model of McCafferty⁹ for the Fe/Cu system in saline environments.

Materials

The galvanic couple was constructed of 6.35 mm dia. Marz grade iron and 50.8 mm dia. Marz grade copper obtained from MRC Inc., Orange, N. J. The iron anode was pressed into a centrally located hole in the copper cathode to produce a cylindrically symmetrical planar galvanic couple. The couple was metallographically polished to an optical finish using standard polishing techniques with the final finish being accomplished with $1.0 \mu\text{m}$ diamond paste.

Electrochemical Measurements

Testing was performed in open cells in laboratory air. All electrochemical measurements were made using 0.6M NaCl electrolytes prepared with reagent grade chemicals and distilled water. Two pH levels were used: 6.5 and 1.75. The pH was adjusted using HCl. The lower pH was used to prevent crevice activity at the Fe/Cu interface. The solution conductivity, σ , was $\sim 0.063 (\Omega\cdot\text{cm})^{-1}$.

The vibrating probe measurements were performed at the Brookhaven National Laboratory in collaboration with H. Isaacs. The test arrangement consisted of a modified vibrating electrode probe assembly and a probe power supply from the Vibrating Probe Company, Davis, California. A Princeton Applied Research Model 5204 lock-in amplifier and a Hewlett Packard 9845B minicomputer with a Hewlett Packard 2240 data acquisition system were used to collect and analyze the data. Mechanical positioning of the probe in the X-Y

plane parallel to the specimen surface was achieved using stages mounted at right angle to each other and driven by two stepping motors under HP9845B computer control.

The vibrating probe tip was positioned above the surface of the couple. Two electrode position heights were used: 650 μm and 1150 μm above the surface of the specimen. The reference electrode was positioned approximately 1 cm above the surface and to the side where no significant current densities were present. The signal from the two electrodes was fed to the differential inputs of the lock-in amplifier. The quadrature was eliminated by adjusting the phase angle to account for the time variation of the vibrating electrode potential. The real component of the vibrating electrode potential was then measured at the extremes of the vibration stroke and the difference in potential was fed to the computer to be processed. The voltage difference was recorded at predetermined grid points and mapped using the graphics capabilities of the HP9845B. These values were then converted to normal ionic current density, J_z , using eq(1). Additional details of the SVET appear in reference¹⁸.

Potentiostatic polarization curves of specimens taken from the copper and iron rods were made using a PAR model 173 potentiostat in combination with a PAR model 175 universal programmer at a stepping rate of 0.1 mv/sec. Standard ASTM G5-78 methods were used.

RESULTS AND DISCUSSION

Electrochemical Measurements

Anodic and cathodic potentiostatic polarization curves for the uncoupled iron and copper in 0.6M NaCl electrolyte at pH levels of 6.5 and 1.75, are shown in Figure 2.

The electrode potential of the galvanic couple as a function of radial distance is shown in Figure 3a. These results can be compared with the experimental data of Rosenfeld in 0.1M NaCl electrolyte at pH=7 and the calculated results of McCafferty from an analytical formulation (Figure 3b). In comparing Fig. 3a and 3b, it should be noted that the experimental conditions were somewhat different in both pH and NaCl concentration of the electrolyte. Even so, the behavior is similar.

Isometric and contour maps of the local ionic currents normal to the corroding Fe/Cu galvanic couple, J_z , are shown in Figures 4 through 6. The ionic currents flowing from the iron are readily discernible in the figures. Figures 4 and 5 show the ionic currents from the couple in pH 1.75 electrolyte with the probe positioned at 650 μm and 1150 μm above the surface of the galvanic couple, respectively. Figure 6 shows the ionic currents measured in pH 6.5 electrolyte at 650 μm above the surface of the couple. Crevice activity is readily discernible at the Fe/Cu interface. The magnitude of J_z is seen to increase appreciably due to the presence of the crevice.

Cross-sectional profiles of normal ionic current density as a function of radial distance from near the centerline of the couple at pH 1.75 are shown in Figures 7 and 8. The profiles model are compared with the finite element

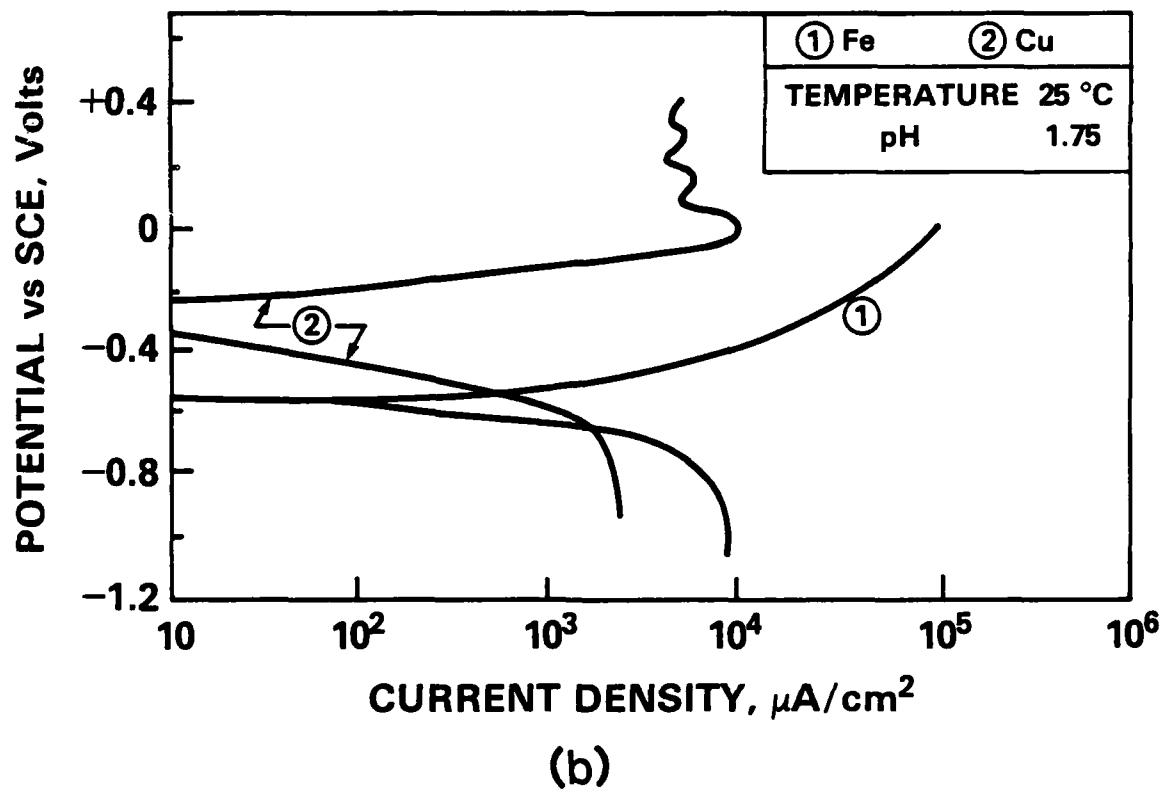
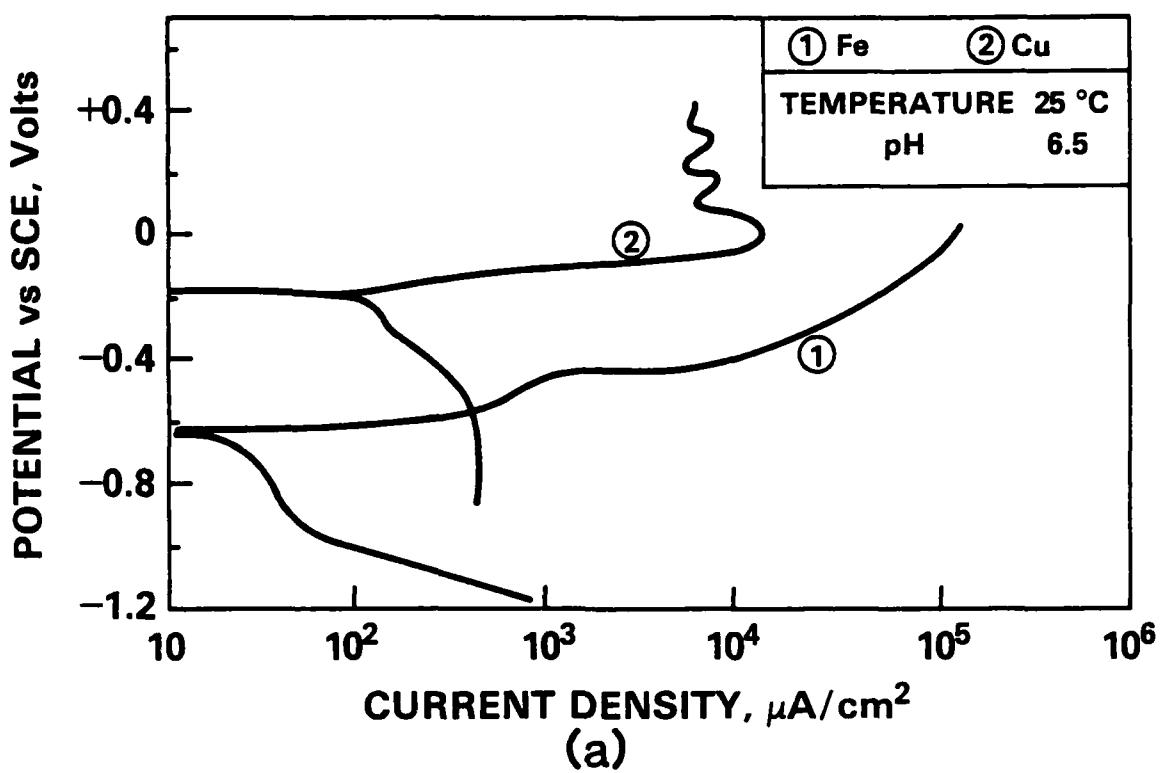
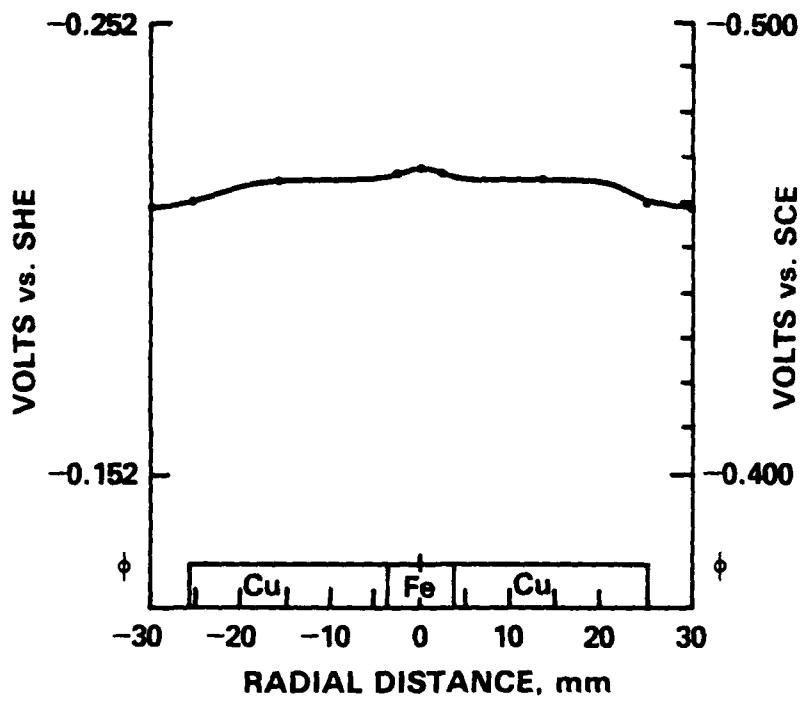
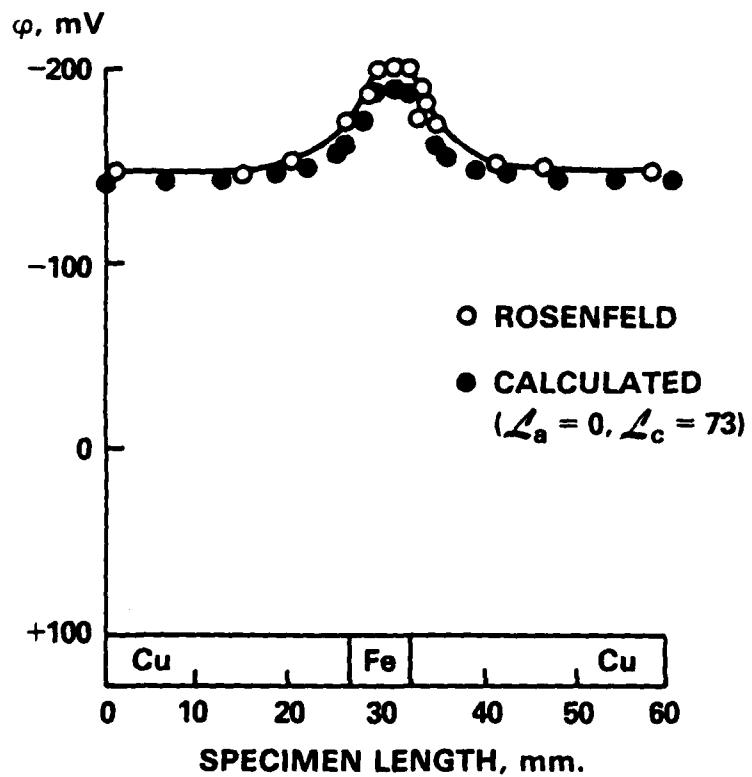


Fig. 2 - Potentiodynamic polarization curves for iron and copper constituents of the galvanic couple at a) pH = 6.5 and b) pH = 1.75



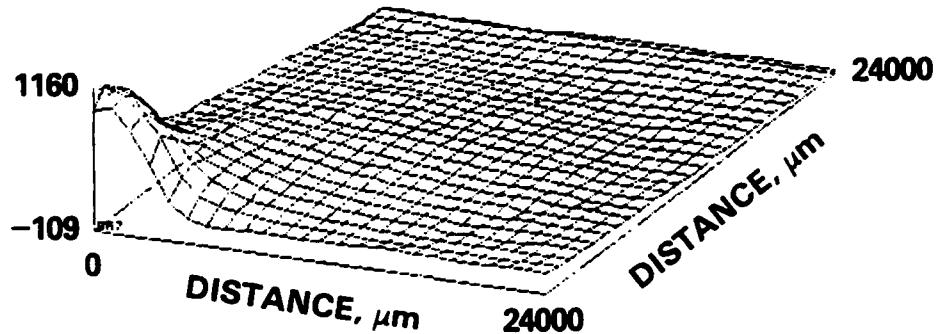
(a)



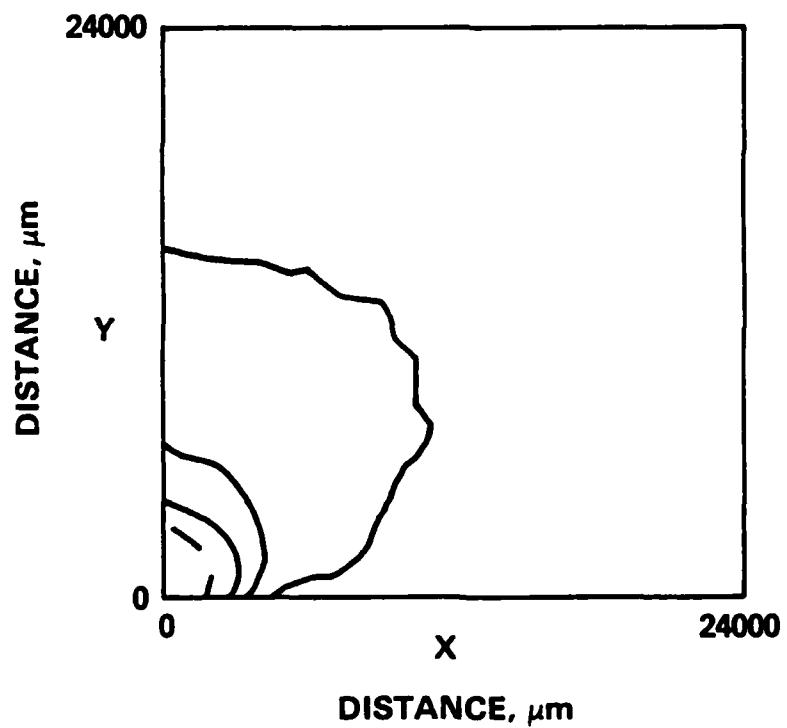
(b)

Fig. 3 - Farfield galvanic couple potential a) as measured and b) from McCafferty, Ref. 9

ANODIC CURRENT DENSITY,
 $\mu\text{A}/\text{cm}^2$



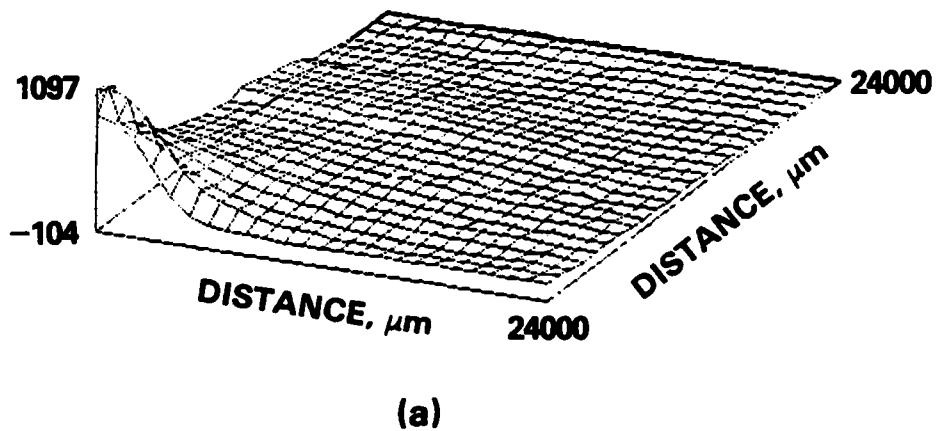
(a)



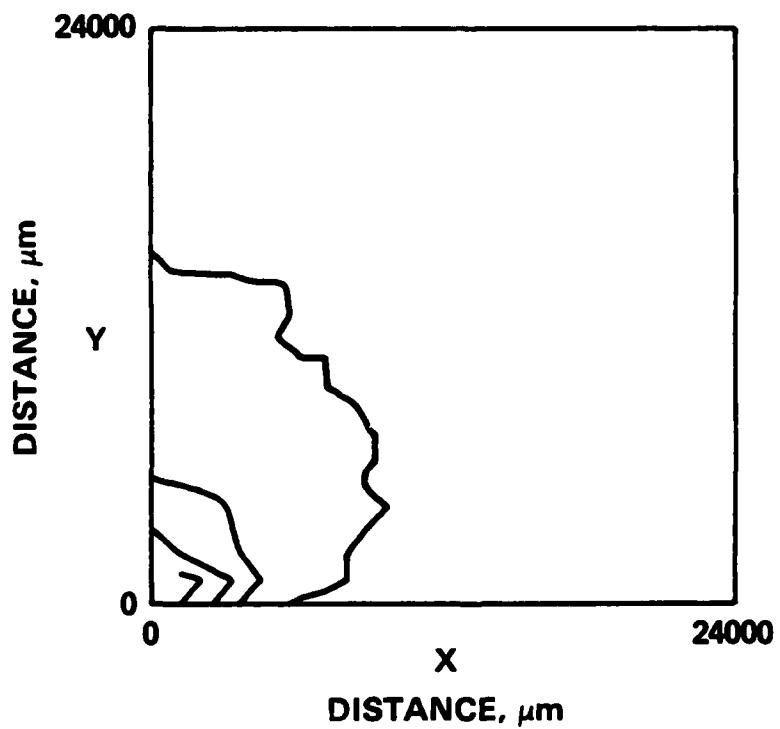
(b)

Fig. 4 - Measured ionic currents at pH = 1.75 at 650 μm above galvanic couple
a) isometric view and b) planar view

ANODIC CURRENT DENSITY,
 $\mu\text{A}/\text{cm}^2$



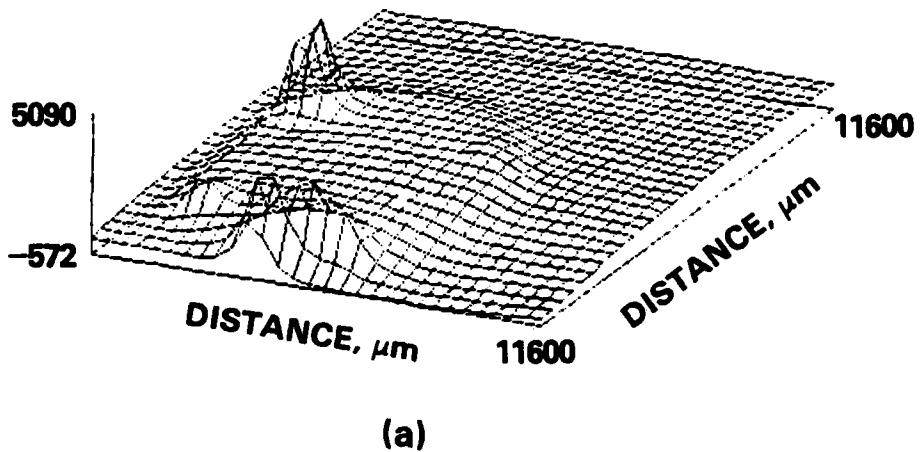
(a)



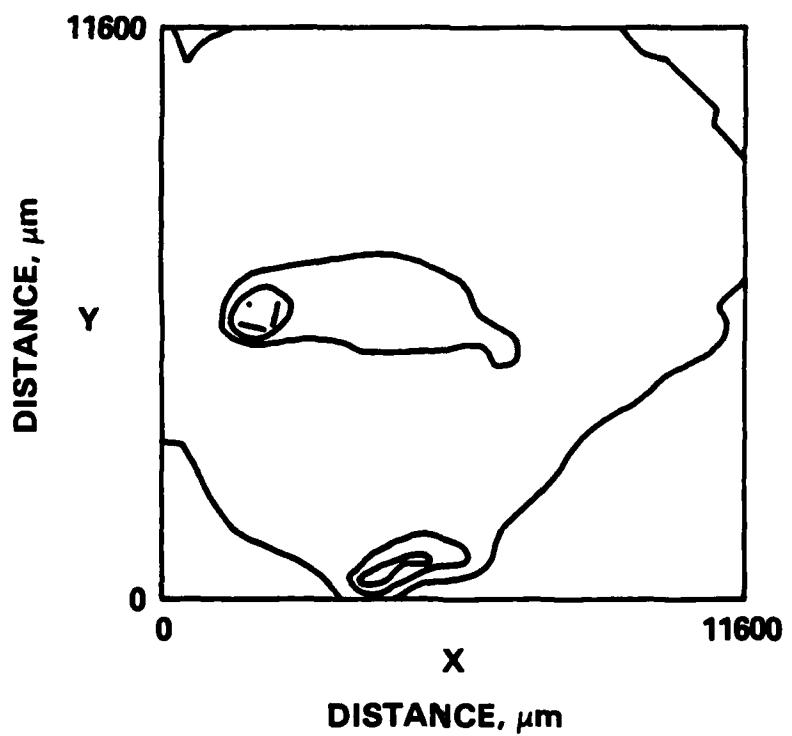
(b)

Fig. 5 - Measured ionic currents at pH = 1.75 at 1150 μm above galvanic couple
a) isometric view and b) planar view

ANODIC CURRENT DENSITY,
 $\mu\text{A}/\text{cm}^2$



(a)



DISTANCE, μm

(b)

Fig. 6 - Measured ionic currents at pH = 6.5 at 650 μm above galvanic couple showing crevice activity: a) isometric view and b) planar view

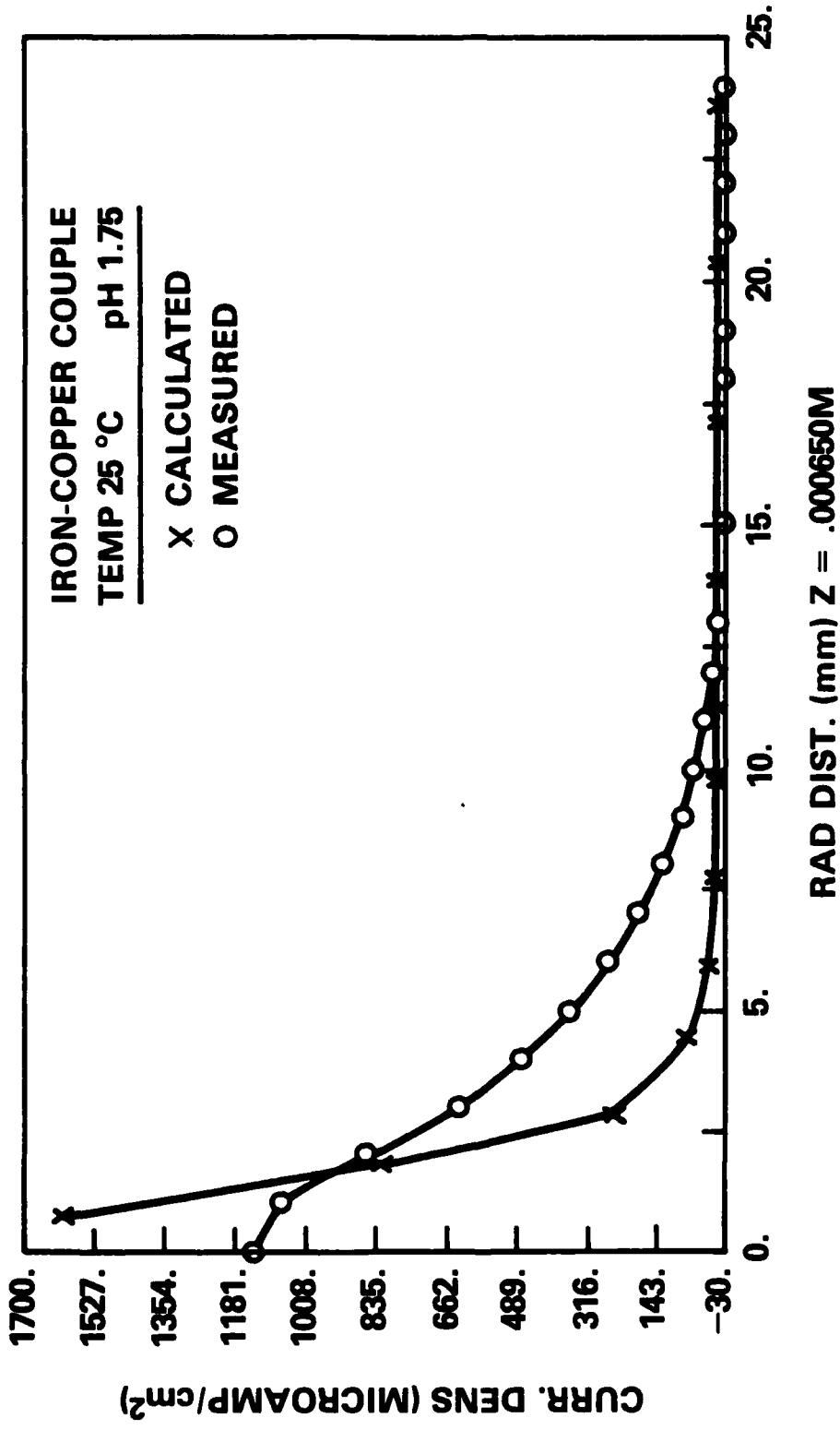


Fig. 7 - Comparison of calculated and measured ionic current density as a function of radial position at pH = 1.75 at 650 μm above galvanic couple

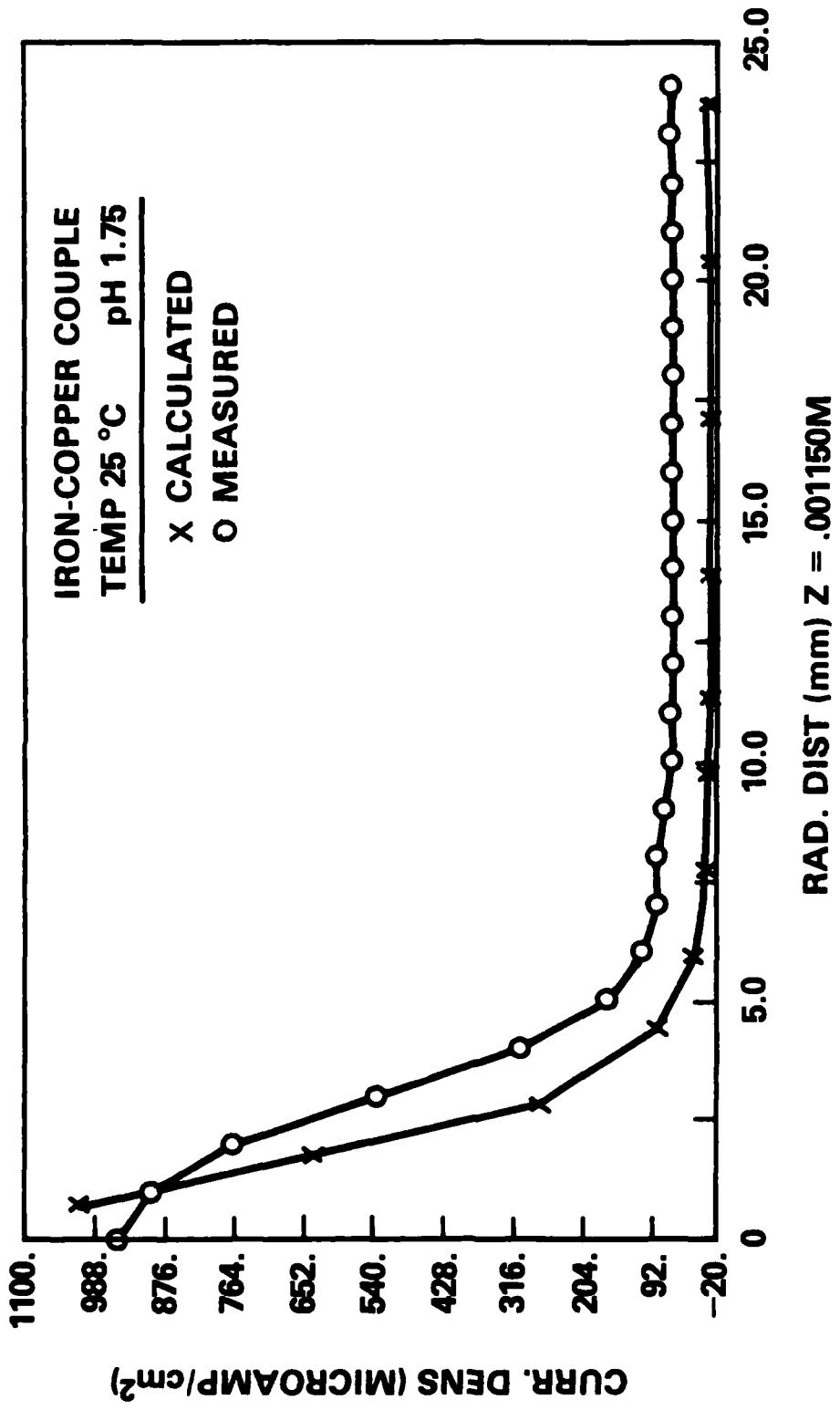


Fig. 8 - Comparison of calculated and measured ionic current density as a function of radial position at pH = 1.75 at 1150 μm above galvanic couple

predictions of J_z using the polarization curves of Fig. 2 and the double membrane model of Kasper and Duffy. The finite element calculations were performed at NUSC/New London by R. Kasper²⁰. As can be seen, agreement between the measured J_z and calculated J_z is quite good in spite of the inherent limitations of the measurement technique. These limitations will be discussed in a later section. A comparison of the finite element predictions with the measurement at $r=0.7\text{mm}$ is shown in Fig. 9. Again, agreement is excellent.

A calculation to compare the measured J_z with the corrosion current density as derived from Fig. 2 was made by assuming that the magnitude of J_z at the peak position is equal to the magnitude of J . The data for J_z at 1150\mu m and at 650\mu m were fitted to an extrapolation function derived from McCafferty's analytical results⁹ to obtain the ionic current density at the surface of the iron electrode. It was further assumed that all the ionic current in the electrolyte which was measured was due to Fe^{+2} ions streaming from the source. The extrapolation function was a two parameter fit to the relation.

$$\phi(r,z) = C_0 + \sum_{n=1}^{\infty} C_n J_0(\lambda_n r) e^{-\lambda_n z} \quad (5)$$

where C_0 and C_n are coefficients, J_0 is the Bessel function of order zero, and $\lambda = \lambda_n/c$, in which the λ_n are the zeros of $J_1(x) = 0$ and c is the radius of the copper cathode. Now at constant $r = r_0$.

$$J(r,z)|_{r_0} = -\sigma \left[\frac{\partial \phi(r,z)}{\partial z} \right]_{r_0} \quad (6)$$

or,
$$J(r_0,z) = \sigma \sum_{n=1}^{\infty} \lambda_n C_n J_0(\lambda_n r_0) e^{-\lambda_n z}|_{r_0} \quad (7)$$

Taking a two parameter fit to eq. (7) and evaluating $J(r,z)$ at $r=0$, $z=0$ gives $J(0,0) = 1263\text{\mu A/cm}^2$. This compares with 5350\mu A/cm^2 derived from Fig. 2. Graphical extrapolation of the FEM predictions to the source in Fig. 9 predicts the source strength to be $\sim 2250\text{\mu A/cm}^2$. This agreement is considered to be good.

Limitations of the Methods

There are several limitations to the vibrating probe technique which should be discussed. First, in order to obtain quantitative current density at the surface of the sample, an extrapolation procedure to account for field fall-off from the central point of measurement to the surface is necessary. The procedure for this extrapolation is not straightforward because the extrapolation function is dependent upon the source strength and the location of the anodes and cathodes on the sample surface. In the simple case of a single point current source (i.e., a small diameter pit) the current falls off as the

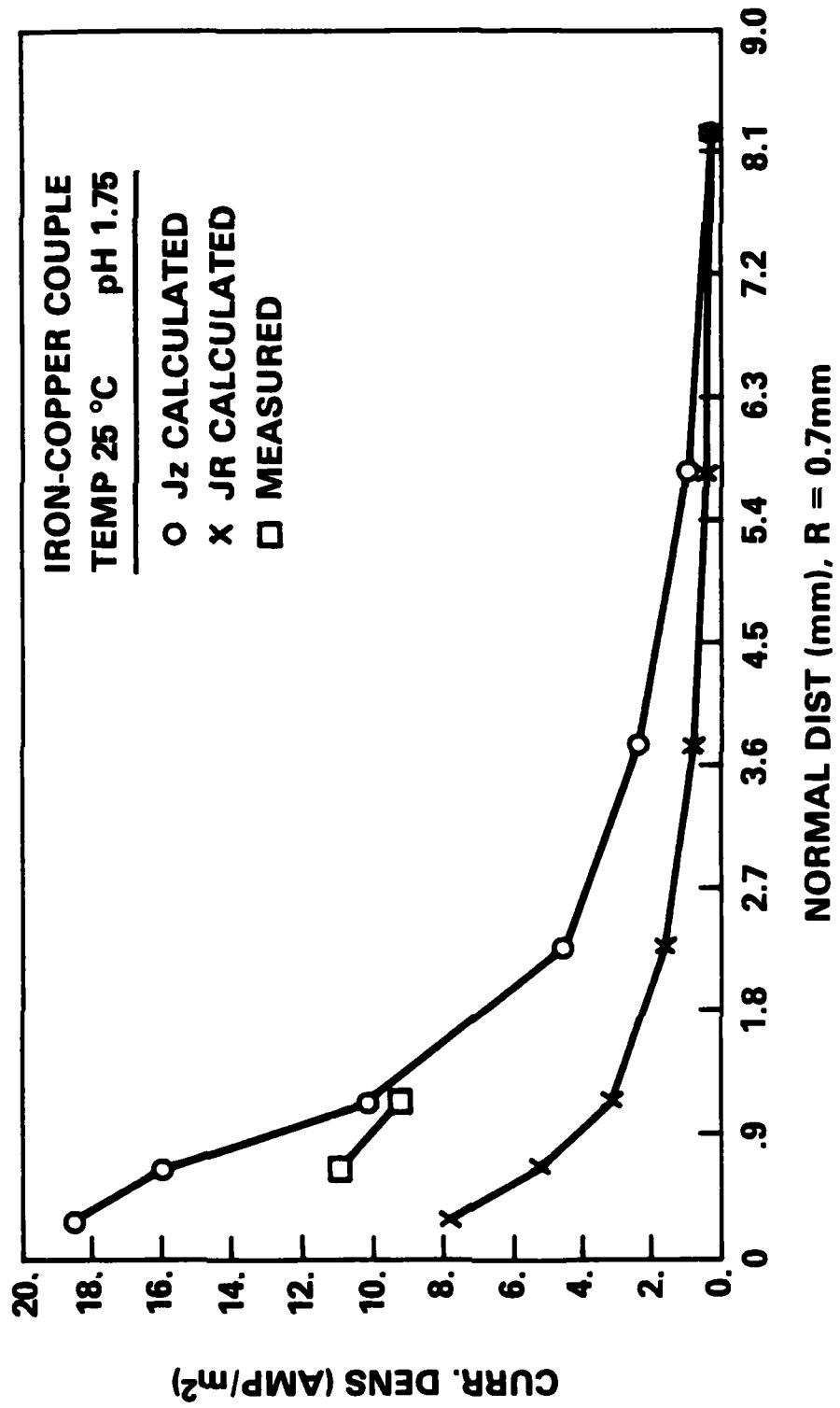


Fig. 9 - Measured ionic current density as a function of height above galvanic couple compared with calculated vector components at $\text{pH} \approx 1.75$

inverse square of the distance. If the current source is an embedded disk, the current falls off exponentially with the distance. In the general case, the extrapolation function depends on the local geometry of the anodes and cathodes and it is unlikely that analytical or finite element solutions to obtain extrapolation functions will be available. Therefore, an experimental measure to obtain an extrapolation function is required to obtain quantitative values for the current density at the specimen surface. This problem holds for measurements made from all external probes.

Another major limitation of the 1-D vibrating probe technique is that only the component of the current parallel to the line of oscillation is measured. In general, ionic current flow in the electrolyte is governed by the three dimensional law of conservation of charge. In differential equation form this law, in the absence of diffusion and convection, can be stated as

$$\nabla \cdot \mathbf{J} = -\frac{\partial \rho}{\partial t} \quad (8)$$

The constitutive relationship (Ohm's Law) between current density and the electric field intensity in terms of the electrical conductance is

$$\mathbf{J} = \sigma \mathbf{E} \quad (9)$$

where by definition, the electric field intensity is

$$\mathbf{E} = -\nabla \phi \quad (10)$$

Substituting equations (10) and (9) into (8) yields

$$\nabla \cdot \sigma \nabla \phi = -\frac{\partial \rho}{\partial t} \quad (11)$$

Therefore, a three-dimensional spatial representation of the ionic current and the local value of the electrolyte conductivity is needed to obtain a general characterization of the corrosion cell. Since the probe used to obtain the data is one dimensional, it would be necessary to change the relative orientation of the probe and the sample to obtain all three orthogonal components of the ionic current. Experimentally, this is difficult to accomplish, time consuming, and leads to uncertainties regarding the location of the current measurement. It can also lead to errors if the magnitude or direction of the current is changing with time. Furthermore, the method does not measure the local value of the electrolyte conductivity so a bulk measurement must be used.

It should be pointed out, however, in spite of these limitations, the one and two dimensional probe methods provide a great deal of useful information in situations where the source location is known and a reasonable extrapolation function can be postulated.

DEVELOPMENT OF A THREE DIMENSIONAL PROBE

In order to fully characterize corrosion microcells, the one and two-dimensional methods must be extended to three-dimensional measurements in

order to map the total ionic current flux at a point in the electrolyte. Scanning the X-Y plane parallel to the surface can then determine the location of the ionic source on the metal surface. In order to accomplish this goal, an electrode based on the two-dimensional probe is being designed and built under contract by J. Freeman and J. Wikswo. Two designs are being investigated, the first design uses three orthogonal linear drives, each of which is aligned with the edge of an imaginary cube. A single tungsten microelectrode is mounted at the intersection of these three drive axes by a stiff insulated stainless steel wire, forming one vertex of the cube. The main diagonal of the cube through that vertex is vertical, so that when viewed from the top the three drives are radially spaced 120° apart. In its simplest mode of operation, two axes vibrated with sine and cosine voltages while the third held stationary to serve as a support. By sequencing through the three permutations of the axes, three sequential measurements made of the current density in the three face planes. The drive and analysis software therefore identical to that already used for the two-dimensional probe, except that any redundant measurements of potential gradients averaged.

The second possible drive technique involves simultaneous oscillation of all three axes at two or three different frequencies to allow simultaneous rather than sequential measurement of all three current density components. The feasibility of this approach will be determined in part by the accuracy with which the electrode position can be controlled, and by possible mixing of the drive frequencies between orthogonal drive directions.

The conductivity of the electrolyte in the vicinity of the recording electrode can be measured by recording the current density that is produced by injecting a known steady current into the electrolyte near the probe tip. Knowledge of the geometry and the injected current allows determination of the conductivity of the medium from the measured current density using Laplace's equation. This type of conductivity determination has already been used in current density analysis developed at Vanderbilt by Freeman and Nicholson.²¹

Acknowledgments

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